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Impurity effects on the mechanical behavior of GaAs crystals

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Effects of In, Zn, and Si impurities on the mechanical behavior of GaAs are investigated. Experimental results are interpreted in terms of the impurity effect on the dislocation velocity and of dislocation locking due to impurities which have been clarified by previous experiments. It is shown that in the temperature range lower than about 600 °C the impurity effect on the dislocation mobility in glide motion plays a dominant role in determining the mechanical strength, while in the higher temperature range dislocation locking by impurities controls the strength. Thus, Si impurity is the most effective in enhancing the strength in the low-temperature range while In impurity is so in the high-temperature range. The dislocation processes which take place during plastic deformation of any impurity-doped GaAs crystals in the low-temperature range are essentially the same as those taking place in highly pure crystals of other kinds of semiconductors such as Ge and Si.

I. INTRODUCTION

Impurity effect on the mechanical strength has long been one of the main topics in the study of mechanical behavior of crystalline materials in terms of the dislocation theory. In spite of an intense and long lasted discussion, however, no complete theory has yet been established which can successfully account for a variety of observed facts on the impurity effect in a consistent and quantitative way. The impurity effect has commonly been discussed in terms of the interaction between a dislocation and impurity atoms, and the stress necessary to make a dislocation overcome the resistance originating from the dislocation–impurity interaction has customarily been assumed to give the magnitude of yield strength of an impure crystal.[1] In most kinds of materials it is very difficult to perform experiments which reveal directly how any given kind of impurity affects the dynamic characteristics of individual dislocations in a crystal as a function of the temperature in a quantitative way. So, there is practically no direct way to verify the validity of theoretical results on dislocation–impurity interaction with experimental observations. Yielding of a crystal is controlled by a number of dislocation processes, such as generation, motion, and multiplication of dislocations, as well as dislocation interaction with various kinds of defects including dislocations themselves. Thus, the characteristics in dislocation–impurity interaction in any crystal may not be related to the macroscopically observable yield strength of the crystal in such a simple way that has customarily been assumed even if the theory could give a correct information on the former.

As in other kinds of materials, the mechanical strength of a semiconductor at an elevated temperature is known to be affected strongly by the presence of impurities. This effect is now widely applied in practice to the electronic device technology. Si crystals containing oxygen impurity at a concentration of about 10^{18} atoms/cm^3 are being used as the materials for integrated circuits because of their smaller susceptibility to the occurrence of wafer warpage caused by thermal stress related to device-production processing in comparison with oxygen-free Si.

Semiconductors are advantageous over other kinds of materials in the study of dislocation–impurity interaction from the view that the dynamic behavior of individual dislocations can directly be investigated in detail experimentally by means of x-ray topography or the etch pit technique because of low densities of dislocations involved. Indeed, direct observations by means of *in situ* x-ray topography have verified that the dislocation velocity in Si at elevated temperatures is little affected by the presence of oxygen impurity and that originally fresh and mobile dislocations become immobile after they are kept at rest at elevated temperatures in oxygen-doped Si.[2–4] Thus, without ambiguity, the strengthening of a Si crystal due to oxygen doping has been concluded to originate in the locking of dislocations and not in the reduction of the dislocation mobility due to oxygen impurity.[5,6] The stress–strain behavior in the yielding of a Si crystal, measured experimentally as a function of the temperature, strain rate, and the density of dislocation sources,[7] has successfully been described quantitatively with a dislocation model which is derived from the results of direct observations on various dislocation processes in Si.[8] The locking of dislocations due to oxygen impurity in Si has been shown to give rise to the same effect on the yielding of a crystal as the reduction in the density of dislocation sources does, which results in an increase in the upper yield stress.[5,6]

The impurity effect on mechanical strength plays an important role also in GaAs crystals. It has empirically been known that doping of certain kinds of impurities is effective in reducing the density of grown-in dislocations in GaAs.[9–12] Doping of a high concentration of In impurity has made it possible to grow a GaAs crystal of a diameter as large as 3 or 4 inches which is essentially free from dislocations.[13,14]

The effects of various kinds of impurities on the dynamic behavior of dislocations in GaAs crystals have been investigated in some detail. The present authors have

TABLE I. Main impurities in the crystals.

Crystal	Impurity	Concentration (atoms/cm^{-3})	Growth technique
undoped	Si	4×10^{15}	Boat
GaAs:Si-1	Si	1×10^{17}	Boat
GaAs:Si-2	Si	4×10^{18}	Boat
GaAs:Zn	Zn	2×10^{19}	Boat
GaAs:In	In	2×10^{20}	LEC

shown that a variety of impurities in GaAs immobilize dislocations on segregating along the latter.[15–19]

It has also been reported that in a certain temperature range electrically active impurities affect the velocity of dislocations in motion[17–23] while isovalent impurities do not.[18] Any given kind of impurity gives rise to different effects on different types of dislocations, such as α, β, and screw dislocations, with regard to both the dislocation mobility and locking. Generally, the impurities which are effective in locking dislocations are not necessarily effective in reducing the dislocation mobility.[18] Most mechanical characteristics of undoped GaAs have been found to be very similar to those of highly pure Si.[24] This shows that various dislocation processes as well as dynamic characteristics of individual dislocations which control the mechanical properties are essentially similar in Si and GaAs.

Up to now, some number of papers have appeared concerning the solution hardening in semiconductors.[25–37] Recently papers have been published specially focusing on the effect of In impurity on the mechanical strength of GaAs in conjunction with the reduction in the density of grown-in dislocations in GaAs due to the doping of In impurity.[31–37] Unfortunately, however, the discussion in these papers seems not correctly to take into account the dislocation processes which determine the yield strength of the crystal as well as the characteristics in the dislocation–impurity interaction in semiconductor crystals at high temperature. The purpose of the present paper is to show how the peculiar effects of impurities on the dynamic behavior of dislocations in GaAs known experimentally are reflected in the dislocation processes which take place in the deformation of a GaAs and, in turn, in the macroscopic mechanical properties of the crystal.

II. EXPERIMENT

Specimens were prepared from GaAs crystals grown by either the boat technique or the liquid encapsulated Czochralski (LEC) technique. Table I shows the species and concentrations of the main impurities involved in the crystals used in the experiments.

The effects of various impurities on the mechanical strength of GaAs were investigated by means of compression tests of specimens under a constant strain rate at elevated temperatures in the atmosphere of highly pure argon gas. Specimens were of a rectangular shape, approximately $2.6 \times 2.6 \times 10.6$ mm^3 in size, with the compression axis along [123].

It is known that the mechanical behavior of a semiconductor crystal depends rather sensitively on the density of mobile dislocations involved in the crystal prior to a deformation test. Thus, for the purpose of obtaining specimens of dislocation densities higher than that of grown-in dislocations, some specimens prepared from the crystals of as-grown state were first subjected to preliminary compression and, then, were annealed at 1050 °C for 24 h in the ambient arsenic gas of the equilibrium pressure followed by rapid cooling.

The geometry of the specimen as well as the details of the experimental procedure are described elsewhere.[24]

III. RESULTS

A. Stress–strain characteristics as dependent on the temperature

The yield strengths of the specimens of both undoped and impurity-doped GaAs in Table I are all measured to show no detectable dependence on the density of dislocations involved prior to the deformation test. Since it is well established that the yield strength of most semiconductors depends very sensitively on the density of dislocation sources involved in a specimen,[7,8] the above observation implies that grown-in dislocations and dislocations annealed at 1050 °C are mostly immobilized by residual or intentionally doped impurities in both the undoped and impurity-doped specimens. Most probable dislocation sources are some kind of irregularities on the specimen surface which are introduced by some unknown processes.[24]

Figure 1 shows the stress–strain curves of various GaAs crystals shown in Table I at a relatively low temperature of 500 °C under a shear strain rate of 2×10^{-4} s^{-1}. All the specimens deformed homogeneously and no inhomogeneous deformation such as the propagation of Lüders bands took place. As in the case of undoped GaAs previously reported,[24] the stress–strain curves of all the specimens are characterized by a noticeable drop in the stress after yielding followed by a gradual increase in the stress with the strain due to work hardening. Thus, we may conclude that the dynamic characteristics of dislocations in GaAs doped with various impurities shown in Table I are essentially similar to those in undoped GaAs at this temperature. They are also similar to those in Ge,[38–42] Si,[7] and GaP[43] at rather low temperatures. It is seen in Fig. 1 that both the upper yield stress and the flow stress after yielding in GaAs: Si-2 are far higher than those in the other kinds of specimens. The increase in the yield stress of GaAs due to Si doping was reported also by other groups.[27–30]

The situation is found to be quite different in deformation at a higher temperature under a low strain rate. Figure 2 shows the stress–strain curves of GaAs:Si-2, GaAs:Zn, and GaAs:In at 900 °C under a shear strain rate of 2×10^{-5} s^{-1}. No specimen shows the stress drop after yielding. The stress–strain curve of GaAs:In has many fine serrations. This is in agreement with the observation of Djemel, Castaing, and Duseaux.[37] It is to be noted that the flow stress of GaAs:In is noticeably higher than those of

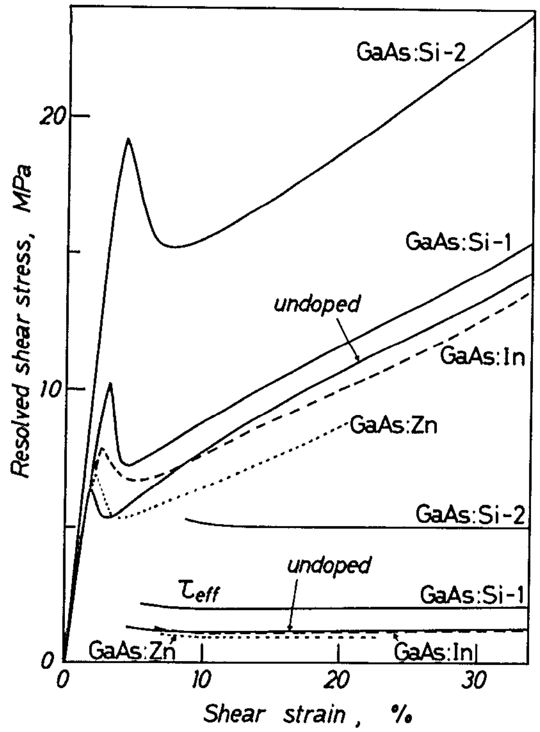

FIG. 1. Stress-strain curves of various GaAs crystals in Table I in compressive deformation at 500 °C under a shear strain rate of 2×10^{-4} s^{-1}. The initial densities of dislocations in all the crystals are about 3×10^{6} cm^{-2}. The effective stress τ_{eff} determined by the strain rate cycling tests is also shown as a function of the strain.

GaAs:Si-2 and GaAs:Zn. Higher yield strength of In-doped GaAs in comparison with that of undoped GaAs at high temperature has been reported also by other groups.[32-36] The serration on stress–strain curve of GaAs:In seen in Fig. 2 is known as the Portevin–LeChatelier phenomenon, and has been observed with other kinds of semiconductors, Si (Ref. 25) and Ge (Ref. 26), which are heavily doped with certain kinds of impurities. The phenomenon has been interpreted to be caused by the dynamical interaction of moving dislocations with migrating impurities though its detailed mechanism has not yet been fully clarified. The stress–strain curve of GaAs:Zn also shows fine serration which is much less remarkable than in GaAs:In.

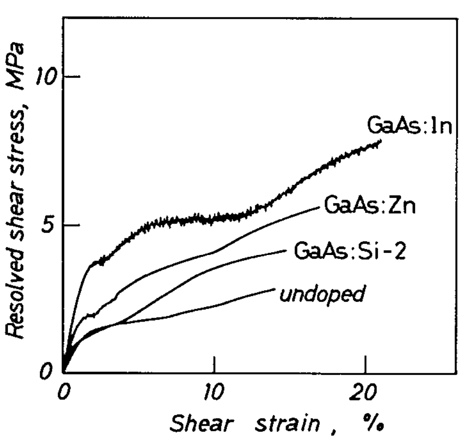

FIG. 2. Stress-strain curves of various GaAs crystals in compressive deformation at 900 °C under a shear strain rate of 2×10^{-5} s^{-1}.

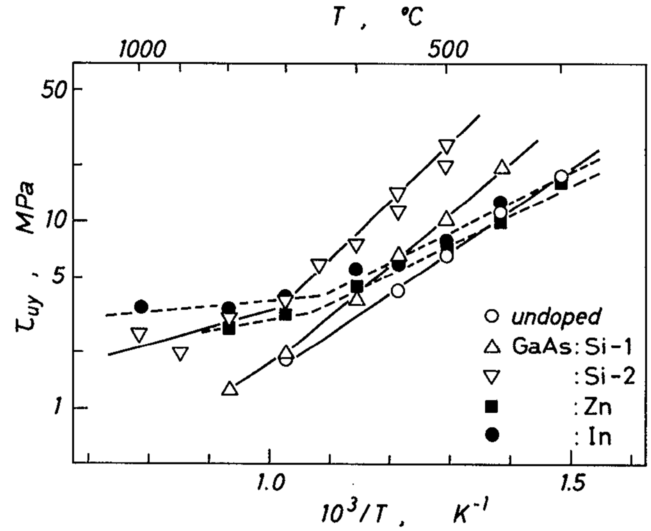

FIG. 3. Upper yield stress τ_{uy} of various GaAs crystals plotted against the reciprocal temperature $1/T$ for a shear strain rate of 2×10^{-4} s^{-1}.

One may interpret the fine serrations on the stress–strain curves in Fig. 2 to be related to the evaporation of volatile arsenic from the specimen surface at high temperatures. The evaporation may cause the roughness of the surface and may induce effective generation centers for dislocations. Such interpretation was eliminated from the following experiment.

Some GaAs:In specimens were deformed at 900 °C under a shear strain rate of 2×10^{-4} s^{-1} in a vacuum, in an ambient arsenic gas of the optimum pressure, or in an ambient argon gas of two atmospheric pressure. The morphology of the specimen surface after deformation was observed to be strongly influenced by the ambient atmosphere. The surface of the specimen deformed in a vacuum was very rough and pieces of molten gallium were found on it. Irrespective of the difference in the surface morphology, the stress–strain curves of the GaAs:In specimens all accompanied serrations in essentially the same manner. Together with the observation that specimens of undoped GaAs and GaAs:Si-2 accompany no detectable serrations, we conclude that the serrations observed in the deformation at high temperatures are caused by dislocation–impurity interaction and not by surface roughening caused by evaporation of arsenic.

B. Yield strength

Figures 3 and 4 show the upper yield stress τ_{uy} and the lower yield stress τ_{ly}, respectively, as a function of the reciprocal temperature for deformation of GaAs shown in Table I under a shear strain rate of 2×10^{-4} s^{-1}. In a specimen showing no stress drop after yielding, the upper yield stress and the lower yield stress are regarded to coincide to each other. In such a case the yield stress is

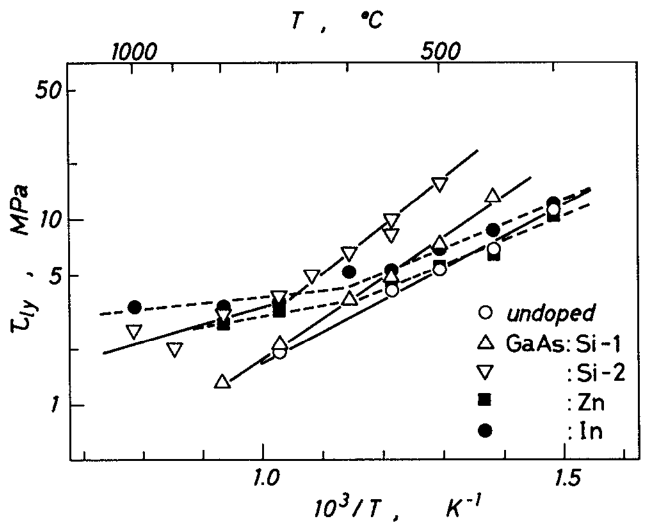

FIG. 4. Lower yield stress τ_{ly} of various GaAs crystals plotted against the reciprocal temperature $1/T$ for a shear strain rate of 2×10^{-4} s^{-1}.

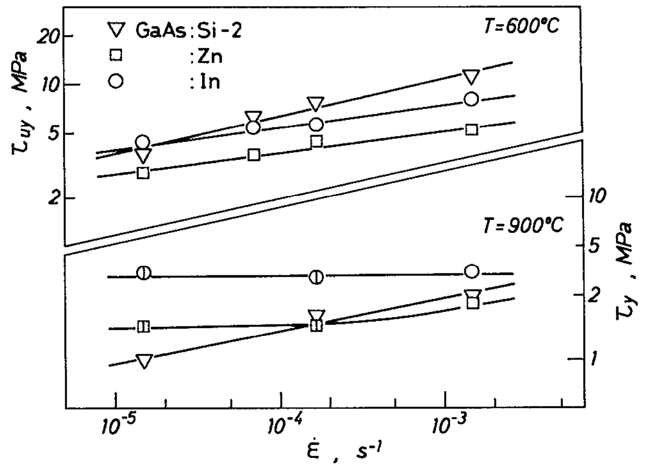

FIG. 5. Yield stresses of the GaAs crystals doped with In, Zn, or Si impurities at 600 and 900 °C plotted against the shear strain rate $\dot{\varepsilon}$. The marks with a vertical line inside mean that the deformation accompanies the Portevin–LeChatelier phenomenon.

defined to be the stress at the intersection of the extrapolation of the initial rise of the stress–strain curve and that of the flat portion after yielding. The temperature dependence of both the upper and lower yield stresses of the impurity-doped crystals is stronger at low temperatures and becomes weaker at higher temperatures. The transition temperature is seen to depend on the species of impurity.

In the low-temperature region, both the upper and lower yield stresses are the highest in GaAs:Si-2 while those of GaAs:In and GaAs:Zn are close to those of undoped GaAs. The yield stresses of Si-doped GaAs increase with an increase in the concentration of Si impurity. The temperature dependence of the upper and lower yield stresses in GaAs:In and GaAs:Zn is weaker than that in the undoped or the Si-doped GaAs. It should be noted that the yield stresses of GaAs doped with Si at a concentration of 1×10^{17} cm^{-3} are higher than those of GaAs doped with Zn or In at concentrations as high as 2×10^{19} or 2×10^{20} cm^{-3}. Both the upper and lower yield stresses depend on the strain rate strongly. A decrease in the strain rate brings about the same effect as an increase in the temperature does.

On the other hand, in the high-temperature region, where yielding is accompanied by no stress drop, the temperature dependence of the yield stress of GaAs:In and GaAs:Zn is much weaker than that of the Si-doped GaAs. As a result, the yield stress of GaAs:In becomes higher than that of the Si-doped GaAs and the yield stresses of GaAs:Zn and GaAs:Si-2 become almost equal. The yield stress of the impurity-doped GaAs depends very weakly on the strain rate in the high-temperature region and is practically constant with respect to the strain rate in GaAs:In and GaAs:Zn. Figure 5 shows the strain-rate dependence of the upper yield stress at 600 °C and that of the yield stress at 900 °C (at which no stress drop is observed after yielding) for GaAs:Si-2, GaAs:In, and GaAs:Zn.

In deformation under a low strain rate a peculiar dependence of the yield stress on the temperature is observed in the impurity-doped GaAs. Figure 6 shows the dependence of yield stress on the temperature in GaAs:In, GaAs:Zn, and GaAs:Si-2 deformed under a strain rate of 2×10^{-5} s^{-1}. A distinct peak of the yield stress is recognized in both GaAs:In and GaAs:Zn at 900 and 800 °C, respectively. The peak is much less distinct in GaAs:Si-2. Stress–strain curves of GaAs:In and GaAs:Zn are characterized by many fine serrations at temperatures around the peak and at higher temperatures. The anomalous temperature dependence of the yield stress in GaAs:In and GaAs:Zn may thus be related to some kind of interaction of moving dislocations with In and Zn impurities at high temperatures.

It is known that the upper and lower yield stresses are well described with a following type of equation as a func-

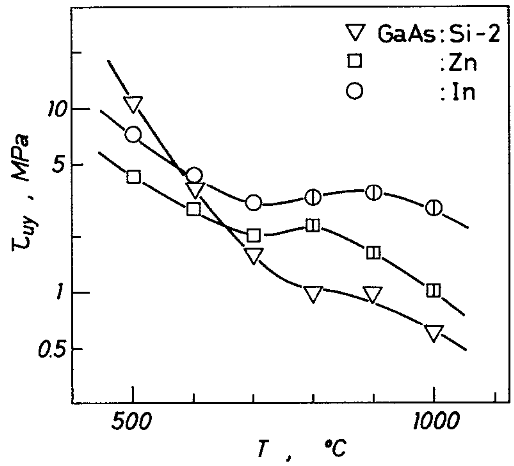

FIG. 6. Yield stress of the GaAs crystals doped with In, Zn, or Si in deformation under a shear strain rate of 2×10^{-5} s^{-1} plotted against the temperature T. Vertical lines inside marks bear the same meaning as in Fig. 5.

TABLE II. Magnitudes of n and U for the upper yield stress τ_{uy} and the lower yield stress τ_{ly} in the low-temperature range.

	τ_{uy}		τ_{ly}	
Crystal	n	U (eV)	n	U (eV)
Undoped	3.6±0.2	0.46±0.05	4.7±0.2	0.33±0.05
GaAs:Si-1	3.8	0.54	4.4	0.44
GaAs:Si-2	4.1	0.61	5.0	0.51
GaAs:Zn	3.6	0.29	4.5	0.25
GaAs:In	4.1	0.26	5.6	0.27

tion of the temperature T and the strain rate $\dot{\epsilon}$ in many kinds of undoped semiconductors such as Si,[7] Ge,[25,26] GaAs,[24] and GaP:[43]

$$\tau = A\dot{\epsilon}^{1/n}\exp(U/kT), \quad (1)$$

where A, n, and U are material constants and k is the Boltzmann constant. It is concluded from the data in Figs. 3 through 6 that in the impurity-doped GaAs Eq. (1) does not hold over the whole temperature and strain rate ranges covered in the present experiment. The expression Eq. (1) is valid in the impurity-doped GaAs only in the low-temperature range. The magnitudes of n and U in such low-temperature range are given in Table II.

C. Effective stress

It is now well accepted that the flow stress of a crystal is divided into two components, the thermal stress and the athermal stress. The former, termed the effective stress, is the stress component to make dislocations overcome some local obstacles or the intrinsic lattice resistance while the latter is the component to make dislocations overcome long range internal stress field in the crystal. The effective stress τ_{eff} can be determined by the strain rate cycling technique described in previous papers in detail.[7,24,40] Figure 1 shows how τ_{eff} changes with the strain for various GaAs crystals together with the flow stress. The density and velocity of dislocations moving during deformation of the crystal can be deduced from the magnitude of τ_{eff} if the expression for the dislocation velocity is known as a function of the stress at the relevant temperature.[7,40,41] Thus, the variation of the magnitude of τ_{eff} with the strain describes how the density and velocity of dislocations change as deformation proceeds. It is seen in the figure that the effective stress in any specimen is constant with respect to the strain in the deformation stage after the lower yield point. This means that both the density and velocity of dislocations in motion are constant against the strain. Such state has been termed the steady state of deformation by Sumino.[42] The steady state has been found to be realized in the deformation of undoped crystals of Ge,[40,41] Si,[7] GaAs,[24] GaP,[43] $GaAs_{0.8}P_{0.2}$,[44] and also in some impurity-doped Si.[45] It is now confirmed that such steady state of deformation is realized in the impurity-doped GaAs in a temperature range 400–600 °C. The steady-state value of the effective stress in any crystal depends on the deformation temperature and the strain rate.

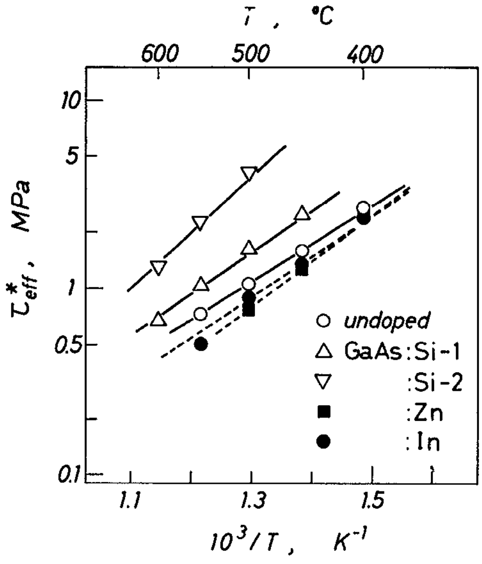

FIG. 7. Steady-state value of the effective stress τ^*_{eff} of various GaAs crystals plotted against the reciprocal temperature $1/T$ for a shear strain rate of $2 \times 10^{-4}\ s^{-1}$.

Figure 7 shows the dependence of the steady-state value of the effective stress in the impurity-doped GaAs on the temperature for a strain rate of $2 \times 10^{-4}\ s^{-1}$ in the temperature region below 600 °C, where no Portevin–LeChatelier effect appears. It is seen in the figure that the magnitude of τ_{eff} of GaAs:Si-2 is the highest and its temperature dependence is the strongest among the others. These characteristics of τ_{eff} have a good correspondence with those of the flow stress of the crystals in the same temperature range. The same is observed also for the dependence on the concentration of Si impurity in the Si-doped GaAs.

The dependence of the steady-state value of τ_{eff} on the temperature T and the strain rate $\dot{\epsilon}$ is well expressed with Eq. (1) with the magnitudes of n and U given in Table III for various GaAs. The result will be discussed in Sec. IV C in connection with the dynamic characteristics of dislocations carrying the deformation.

It is concluded that the characteristics in deformation behavior and the related dynamic state of dislocations of GaAs crystals doped with various impurities in the temperature range below 600 °C are similar to those in undoped GaAs and other semiconductors such as Si, Ge, etc.

TABLE III. Magnitudes of n and U for the steady-state value of effective stress τ^*_{eff}.

	τ^*_{eff}	
Crystal	n	U (eV)
Undoped	3.6±0.2	0.40±0.05
GaAs:Si-1	3.6	0.44
GaAs:Si-2	3.6	0.58
GaAs:Zn	3.7	0.48
GaAs:In	3.5	0.41

IV. DISCUSSION

A. Mechanical strength of impurity-doped GaAs in the low-temperature range

Three types of dislocations, namely dislocations of α, β, and screw types, are activated simultaneously when a GaAs crystal is stressed and undergoes plastic deformation at an elevated temperature. The mechanical property of GaAs is controlled by dynamic behavior of these three types of dislocations. It has been found that different kinds of impurities give rise to different effects on the mobility of each type of dislocation in GaAs. Isovalent impurities such as In and Al give rise to no appreciable effect on the mobility of any type of dislocations at temperatures higher than about 350 °C.[18] This observation is in agreement with a theoretical expectation. The maximum magnitude of the interaction energy between a dislocation and an In atom has been estimated to be 0.666 eV when the In atom is separated from the dislocation by one atomic distance.[31] The interaction energy decreases rapidly with the distance of the In atom from the dislocation. Such magnitudes of the interaction energy never give rise to appreciable increments in the stress that makes a dislocation overcome the resistance of an In impurity atom in the temperature range higher than room temperature as shown in the previous paper.[17] Acceptor-type impurity such as Zn has been found to enhance the mobilities of β and screw dislocations while reducing the mobility of α dislocations.[18–23] The former effect has been interpreted with the idea that a 30° partial dislocation of β type accompanies some donor level. Donor-type impurities such as Si and Te retard the motion of all the types of dislocations in GaAs, resulting in the decrease in their mobilities.[18–23] This retarding effect becomes more pronounced with the increase in the concentration of the donor impurities. Exact mechanisms of such retarding effects are not fully understood. At present, they are tentatively attributed to the development of clusters or complexes including these impurities in GaAs which have rather high energies of interaction with relevant type of dislocations.[18]

All the impurity effects on the dislocation mobility mentioned above are seen to be clearly reflected on the magnitudes of the upper and lower yield stresses as well as on that of the flow stress at any deformation stage of the various GaAs crystals in the low-temperature range given in Figs. 1, 3, and 4. Namely, these stresses of GaAs:In are almost equal to those of undoped GaAs while those of GaAs:Zn are slightly lower. On the other hand, the yield and flow stresses of the Si-doped GaAs are much higher than those of the other GaAs and the effect is observed to be more pronounced with the increase in the concentration of Si impurity.

We may conclude that the impurity effect on the mechanical strength of GaAs in the low-temperature range is controlled by the impurity effect on the dislocation mobility in glide motion. This point will further be discussed in detail in conjunction with the behavior of the effective stress in Sec. IV C. The stress–strain curves of the impurity-doped GaAs in the yield region at a low temperature seen in Fig. 1 assume a shape very similar to those of Si and undoped GaAs. Since the stress–strain curve in the yield region directly reflects both the dynamic feature of dislocations and the multiplication process of dislocations, we reach at the conclusion that the dislocation processes which take place in the deformation of impurity-doped GaAs in this temperature range are essentially the same as those taking place in the deformation of Si and undoped GaAs. A model has successfully been developed for such dislocation processes in Si.[8]

B. Strength of impurity-doped GaAs in the high-temperature range

The yield stress and the flow stress at any deformation stage in both GaAs:In and GaAs:Zn are higher than those in GaAs:Si-2 in the high-temperature range as seen in Figs. 2, 3, and 4. This implies that the factor controlling the relative strengths of these GaAs in the low-temperature range no longer plays an important role in determining their relative strengths in the high-temperature range. Such a factor is thought to be the resistance of impurities or their small clusters dispersed within the crystal against the glide motion of any type of dislocations. The resistance related to Si impurity is the highest among others, resulting in the lowest dislocation mobilities in the low-temperature range. From a theoretical viewpoint there seems to be no plausible reason to expect that the decrease in the resistance to the dislocation motion related to Si impurity with increasing temperature is much more drastic than those related to In and Zn impurities if the impurity atoms are distributed individually on the glide planes of the dislocations. Thus, the model for the hardening of GaAs by In doping proposed by Guruswamy *et al.*[34,35] never accounts for a higher high-temperature strength of the In-doped GaAs in comparison with the Si-doped GaAs.

We have seen that high flow stresses in GaAs:In and GaAs:Zn are accompanied by numerous fine serrations on the stress–strain curves known as the Portevin–LeChatelier phenomenon. A sharp drop in the flow stress at a serration on a stress–strain curve indicates that some macroscopic amount of plastic deformation takes place instantaneously at a rate much higher than the total deformation rate of the specimen given by the deformation machine. Such a rapid deformation leads to a release of the elastic strain of the deformation system and, in turn, results in a sharp drop in the flow stress. To give rise to any detectable amount of stress drop, a certain number of dislocations must move simultaneously at a sufficient high velocity to give rise to a macroscopic strain. If we extrapolate the velocity data of any type of dislocations at low temperatures in the impurity-doped GaAs to high temperatures, we see that the extrapolated velocities under relevant stresses are much higher than the diffusion rate of any kind of impurities. This means that moving dislocations are never caught by diffusing impurities in the high-temperature range.

Transmission electron microscopic observations have revealed that dislocations undergo so-called jerky motion in GaAs when dislocations are highly mobile at a high temperature.[46] Namely, a dislocation is trapped by some obstacle, such as another dislocation, a large cluster of impurities or internal stress, discretely located on the glide plane after some amount of fast glide motion. After being halted there for a while, the dislocation is released from the obstacle with the help of an increase in the applied stress or thermal activation and moves fast along the glide plane until it is trapped by the next obstacle. In the jerky motion of a dislocation this process is repeated.

In the previous paper[18] it was verified experimentally that In impurity segregates on α and screw dislocations even at a temperature as low as about 350 °C and effectively immobilizes these types of dislocations. Immobilization of any type of dislocation due to segregation of Si impurity takes place effectively only at much higher temperatures. This difference reflects the difference in the diffusivities of these two kinds of impurities in GaAs. Zn impurity selectively immobilizes β and screw dislocations and the temperature at which the immobilization takes place effectively is between those for In and Si impurities for the relevant concentrations of the impurities.

We propose the following picture for the strengthening mechanism of GaAs due to doping of In or Zn impurity in the high-temperature range. During deformation dislocations are halted at local obstacles after free-flight motion over certain distances and spend some waiting time before being released to the next free-flight motion, the waiting time being determined by the strain rate. While the dislocations are halted, they getter impurity atoms and become locked. An extra stress is needed to release the dislocations from gettered impurities in addition to the stress to overcome the original obstacles. The efficiency of the locking is higher for impurities with a higher diffusivity. In In-doped GaAs, In impurity atoms segregate rapidly on α and screw parts of the halted dislocations, while Zn impurity atoms segregate on β and screw parts in Zn-doped GaAs. Releasing of dislocations from the gettered impurities enhances the jerky nature of dislocation motion and the process is thought to take place in a cooperative manner, resulting in a sharp stress drop of a macroscopically observable magnitude, namely in the Portevin–LeChatelier phenomenon.

The above picture gives a plausible explanation for the characteristics in hardening of GaAs due to doping of In or Zn. In impurity is the fastest diffuser and Zn impurity is the next among In, Zn, and Si impurities in GaAs. Thus, the effect appears in the most pronounced way in the In-doped GaAs and next in the Zn-doped GaAs. As the temperature is raised, the diffusion rate of impurities increases and gettering takes place more rapidly and, as a consequence, the yield stress is enhanced. With further increase in temperature, however, the release process of locked dislocations will also be enhanced by the thermal activation, resulting in the reduction in the yield stress. Gettering itself is supposed to take place less effectively if the temperature is too high since the impurity state at the dislocation core becomes less stable with increasing temperature. Thus, a peak of the yield stress results at a certain temperature as seen in Fig. 6. The waiting time at an obstacle is shorter for a higher strain rate. The gettering of the impurity atoms at a halted dislocation is less effective within a shorter waiting time. So, the locking of dislocation is weaker. On the other hand, the stress necessary to release a dislocation from any local obstacle with the help of thermal activation increases with increasing strain rate. The reverse holds for a lower strain rate. Thus, the two effects tend to compensate each other in determining the release stress of the dislocation from the locking agents. This gives the reason why the observed yield stress is insensitive to the strain rate in GaAs:In and GaAs:Zn in the concerned temperature range as seen in Fig. 5.

C. Effective stress in the impurity-doped GaAs

The dependence of the steady-state value of the effective stress on the temperature and the strain rate has theoretically been given by Sumino.[42] Since his model is illustrated in a number of papers,[8,24,40–45] the hypothesis in the theory on the state of collective motion of dislocations and the derivation of the related formula are not repeated here.

It is well known that the velocity v of any type of dislocations in both undoped and impurity-doped semiconductors in the relevant temperature range is given by the following empirical equation as a function of the stress τ and the temperature T:

$$v = v_0 \tau^m \exp(-Q/kT), \tag{2}$$

where v_0, m, and Q are material constants and k the Boltzmann constant. The Sumino theory leads to the following relation between n, U in Eq. (1) for the effective stress in the steady state of deformation and m, Q in Eq. (2) for the velocity of an individual dislocation which controls the deformation rate of the crystal:

$$n-2=m, \quad nU=Q. \tag{3}$$

TABLE IV. Magnitudes of m and Q in Eq. (2) for screw dislocations determined from the steady state values of effective stress $\tau^*_{\rm eff}$, from direct measurements of dislocation velocity, and from the lower yield stress $\tau_{\rm ly}$.

Crystal	From $\tau^*_{\rm eff}$		From direct measurements		From $\tau_{\rm ly}$	
	m	Q (eV)	m	Q (eV)	m^*	Q^* (eV)
Undoped	1.6 ± 0.2	1.4 ± 0.2	1.8 ± 0.2	1.4 ± 0.1	2.7 ± 0.2	1.6 ± 0.2
GaAs:Si-1	1.6	1.6	1.8	1.5	2.4	1.9
GaAs:Si-2	1.6	2.0	1.9	1.7	3.0	2.6
GaAs:Zn	1.7	1.7	2.1	1.6	2.5	1.1
GaAs:In	1.5	1.4	1.8	1.3	3.6	1.5

Equation (3) has experimentally been confirmed to hold in Ge,[40,41] Si,[7,45] and undoped GaAs.[24] In III-V compound semiconductors screw dislocations control the deformation rate.[24] Table IV gives the magnitudes of m and Q for screw dislocations obtained by substituting the experimental values of n and U in Table III into Eq. (3) and compares them with those of m and Q directly obtained from the measurements of dislocation velocities in the impurity-doped GaAs.[18] The magnitudes of m and Q obtained from the two different experimental methods agree with each other within the experimental errors. Thus, we may conclude that, as in Ge, Si, and undoped GaAs, the steady state of dislocation motion during deformation proposed by Sumino is realized in the impurity-doped GaAs in the temperature range lower than 600 °C where the mobility of dislocations in glide motion controls the deformation behavior of the crystal. It has been proposed by Haasen[47] that Eq. (1) holds for the lower yield stress of a semiconductor crystal and that n and U there have the relations with m and Q given by Eq. (3). In spite of the fact that a mathematical error in his derivation has been pointed out,[8] the result has sometimes been used to guess the characteristics in the dislocation motion from the measurements of the lower yield stress of compound semiconductors.[33,48] The magnitudes of m and Q obtained by substituting the values of n and U in Table II for the lower yield stress are given in Table IV being denoted as m^* and Q^*. It should be noted that the discrepancies between m and m^* as well as those between Q and Q^* are much larger than experimental errors. This reflects the fact that the magnitude of the lower yield stress is not determined by the dislocation mobility alone but also by the multiplication process.[8]

V. CONCLUSION

The mechanical behavior and the dislocation dynamics in the deformation have been investigated with GaAs doped with In, Zn, or Si impurity. The results are summarized as follows:

(1) The stress–strain characteristics of the impurity-doped GaAs in the temperature range lower than about 600 °C are similar to those of undoped GaAs. In this temperature range the effect of the impurities on the dislocation mobility in glide motion plays an essential role in determining the mechanical strength of the crystal, and Si impurity is the most effective in enhancing the yield and flow stresses.

(2) The Portevin–LeChatelier effect appears in deformation of the impurity-doped GaAs in the temperature range higher than about 600 °C. Dislocation locking by impurities during the jerky motion is concluded to be responsible for this effect and controls the mechanical strength, and In impurity is the most effective in enhancing the strength.

(3) The dynamic state of dislocations in the deformation of the impurity-doped GaAs in the low-temperature range is controlled by the mechanism essentially the same as that in other kinds of undoped semiconductors.

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[1] As a review, P. Haasen and H. Suzuki, *Dislocations in Solids*, edited by F. R. N. Nabarro (North-Holland, Amsterdam, 1979), Vol. 4, pp. 155 and 191.
[2] K. Sumino, H. Harada, and I. Yonenaga, Jpn. J. Appl. Phys. **19**, L49 (1980).
[3] M. Imai and K. Sumino, Philos. Mag. A **47**, 599 (1983).
[4] K. Sumino and M. Imai, Philos. Mag. A **47**, 753 (1983).
[5] K. Sumino, *Defects in Semiconductors II*, edited by S. Mahajan and J. W. Corbett (North-Holland, Amsterdam, 1983), p. 307.
[6] I. Yonenaga, K. Sumino, and K. Hoshi, J. Appl. Phys. **56**, 2346 (1984).
[7] I. Yonenaga and K. Sumino, Phys. Status Solidi A **50**, 685 (1978).
[8] M. Suezawa, K. Sumino, and I. Yonenaga, Phys. Status Solidi A **51**, 217 (1979).
[9] Y. Seki, H. Watanabe, and J. Matsui, J. Appl. Phys. **49**, 822 (1978).
[10] M. G. Mil'vidskii, V. B. Osvenskii, and S. S. Shifrin, J. Cryst. Growth **52**, 396 (1981).
[11] Yu. N. Bol'sheva, Yu. A. Grigor'ev, S. P. Grishina, M. G. Mil'vidskii, V. B. Osvenskii, and S. S. Shifrin, Sov. Phys. Crystallogr. **27**, 433 (1982).
[12] G. Jacob, M. Duseaux, J. P. Farges, M. M. van den Boom, and P. J. Roksnoer, J. Cryst. Growth **61**, 417 (1983).
[13] H. Kohda, K. Yamada, H. Nakanishi, T. Kobayashi, J. Osaka, and K. Hoshikawa, J. Cryst. Growth **71**, 813 (1985).
[14] T. Ibuka, Y. Seta, M. Tanamura, F. Orito, T. Okano, F. Hyuga, and J. Osaka, *Semi-insulating III-V Materials*, edited by H. Kukimoto and S. Miyazawa (Ohm and North-Holland, Tokyo and Amsterdam, 1986), p. 77.
[15] I. Yonenaga, K. Sumino, and K. Yamada, Appl. Phys. Lett. **48**, 326 (1986).
[16] I. Yonenaga, M. Takebe, and K. Sumino, Izv. Akad. Nauk. SSSR, Fiz. **51**, 1480 (1987).
[17] I. Yonenaga and K. Sumino, J. Appl. Phys. **62**, 1212 (1987).
[18] I. Yonenaga and K. Sumino, J. Appl. Phys. **65**, 85 (1989).
[19] K. Sumino, *Point and Extended Defects in Semiconductors*, edited by G. Benedek, A. Cavallini, and W. Schröter (Plenum, New York, 1989), p. 77.
[20] S. A. Erofeeva and Yu. A. Ossipyan, Sov. Phys.–Solid State **15**, 538 (1973).
[21] V. B. Osvenskii, L. P. Kholodyni, and M. G. Mil'vidskii, Sov. Phys.–Solid State **15**, 661 (1973).
[22] S. K. Choi, M. Mihara, and T. Ninomiya, Jpn. J. Appl. Phys. **16**, 737 (1977).
[23] H. Steinhardt and P. Haasen, Phys. Status Solidi A **49**, 93 (1978).
[24] I. Yonenaga, U. Onose, and K. Sumino, J. Mater. Res. **2**, 252 (1987).
[25] H. Siethoff, Phys. Status Solidi **40**, 153 (1970).
[26] H. G. Brion, P. Haasen, and H. Siethoff, Acta Metall. **19**, 283 (1971).
[27] V. Swaminathan and S. M. Copley, J. Am. Ceram. Soc. **58**, 482 (1975).
[28] E. D. Bourret, M. G. Tabache, and A. G. Elliot, Appl. Phys. Lett. **50**, 1373 (1987).
[29] Y. Nakada and T. Imura, Phys. Status Solidi A **103**, 435 (1987).
[30] P. Boivin, J. Rabier, and H. Garem, Philos. Mag. A **61**, 619 (1990).
[31] H. Ehrenreich and J. P. Hirth, Appl. Phys. Lett. **47**, 668 (1985).
[32] H. M. Hobgood, S. McGuigan, J. A. Spitznagel, and R. N. Thomas, Appl. Phys. Lett. **48**, 1654 (1986).
[33] M. G. Tabache, E. D. Bourret, and A. G. Elliot, Appl. Phys. Lett. **49**, 289 (1986).
[34] S. Guruswamy, R. S. Rai, K. T. Faber, and J. P. Hirth, J. Appl. Phys. **62**, 4130 (1987).
[35] S. Guruswamy, R. S. Rai, K. T. Faber, J. P. Hirth, J. E. Clemans, S. McGuigan, R. N. Thomas, and W. Mitchel, J. Appl. Phys. **65**, 2508 (1990).
[36] R. S. Rai, S. Guruswamy, K. T. Faber, and J. P. Hirth, Philos. Mag. A **60**, 339 (1989).
[37] A. Djemel, J. Castaing, and M. Duseaux, Philos. Mag. A **57**, 671 (1988).
[38] H. Alexander and P. Haasen, Solid State Phys. **22**, 28 (1968).

[39] K. Kojima and K. Sumino, Cryst. Lattice Defects **2**, 147 (1971).
[40] K. Sumino and K. Kojima, Cryst. Lattice Defects **2**, 159 (1971).
[41] K. Sumino, S. Kodaka, and K. Kojima, Mater. Sci. Eng. **13**, 263 (1974).
[42] K. Sumino, Mater. Sci. Eng. **13**, 269 (1974).
[43] I. Yonenaga and K. Sumino, J. Mater. Res. **4**, 355 (1989).
[44] I. Yonenaga, K. Sumino, G. Izawa, H. Watanabe, and J. Matsui, J. Mater. Res. **4**, 361 (1989).
[45] K. Sumino, I. Yonenaga, H. Harada, and M. Imai, *Proceedings of the International Conference on Dislocation Modelling of Physical Systems*, edited by M. F. Ashby, R. Bullough, C. S. Hartly, and J. P. Hirth (Pergamon, New York, 1981), p. 212.
[46] M. Sato, M. Takebe, and K. Sumino, *Proceedings of the Yamada Conference on Dislocations in Solids*, edited by H. Suzuki, T. Ninomiya, K. Sumino, and S. Takeuchi (Univ. of Tokyo Press, Tokyo, 1985), p. 429.
[47] P. Haasen, Z. Phys. **167**, 461 (1962).
[48] G. Müller, R. Rupp, J. Völkl, H. Wolf, and W. Blum, J. Cryst. Growth **71**, 771 (1985).